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PROCEEDINGS
OF THE
1970 CONFERENCE
ON
CITRUS CHEMISTRY
AND UTILIZATION

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Held at
Winter Haven, Fla.
October 9, 1970

Agricultural Research Service
UNITED STATES DEPARTMENT OF AGRICULTURE

PREFACE

The Conferences on Citrus Chemistry and Utilization are sponsored by the Southern Marketing and Nutrition Research Division of USDA's Agricultural Research Service to report research developments in the broad area of processing, marketing, and utilization, and to provide for exchange of information that will benefit the industry and future research.

This report summarizes the statements of the various speakers during the Conference, and gives an account of the discussions that followed. If further details are desired regarding any subject presented here, they may be obtained by communicating with the author concerned.

C. H. FISHER, Director
Southern Marketing and Nutrition
Research Division

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Underscored numbers in parentheses refer to references at the end of each article.

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PROCEEDINGS OF THE 1970 CONFERENCE ON CITRUS CHEMISTRY AND UTILIZATION
HELD AT WINTER HAVEN, FLA., OCTOBER 9, 1970
Talcott W. Edminster, General Chairman

Dr. Veldhuis called the conference to order and introduced Talcott W. Edminster, General Chairman, who, on behalf of the Agricultural Research Service, welcomed those in attendance.

SESSION I: James M. Bonnell, Chairman

ANHYDROUS AMMONIA PENETRATION OF CITRUS FRUIT

by

Joseph H. Bruemmer and Bongwoo Roe
Southern Marketing and Nutrition Research Division
U. S. Fruit and Vegetable Products Laboratory
Winter Haven, Fla.

(Presented by Joseph H. Bruemmer)

Anaerobic metabolism of intact fruit decreased juice acidity about 10 percent. Further decrease could not be obtained by varying process parameters of time, temperature, and gas composition. Because citric acid is the major acid of citrus juices, the limited decrease in acidity was thought to be due to metabolic immobility of citric acid.

In citrus fruit citric acid is oxidized aerobically to CO_2 and to compounds that are aminated to amino acids. Stimulation of amination by increasing ammonia availability may increase citric acid oxidation resulting in decrease in juice acidity. Therefore, we examined the effect on juice acidity of treating intact citrus fruit with anhydrous NH_3.

Exposure of Valencia oranges to 10 percent NH_3 in O_2 for 16 hours at 100°F. decreased acidity about the same as exposure to air at 100°F. After 40 hours' treatment, however, acidity of NH_3-treated fruit, had declined 40 percent below the value of air-treated fruit. The total citrate concentration was lower in juice from NH_3-treated fruit, but the difference between treatments was not enough to account for the decline in acidity (table 1). NH_3 treatment darkened the flavedo and albedo and increased albedo juice to pH 8, suggesting that the ammonia penetrated the peel and neutralized some of the citric acid in the vesicles. Exposing oranges to 5 percent NH_3 in N_2 for 3 hours at 100°F. also decreased acidity of juice.

Chemical neutralization was indicated by the following observation. When Valencia oranges were exposed to 100 percent anhydrous NH_3 at 100°F., the titratable acidity declined from 1.01 to 0.24 percent citric acid in 16 hours. The vesicle juice was pH 6.0 and albedo juice was pH 9.0.

Chemical neutralization was slower at 70°F.; 40 hours were required to decrease titratable acidity to 0.26 percent citric acid. About 10 percent decrease in acidity was obtained after 8 hours of exposure to NH_3 at 70°.

Results of these experiments indicate: (1) NH_3 at low concentration in O_2 stimulates citric acid oxidation to decrease titratable acidity by decreasing total citrate concentration; (2) NH_3 at higher concentration chemically neutralizes citric acid in juice vesicles.

NOTE: The use of ammonia on citrus fruit has not been cleared by Federal or State Agencies. For one thing, the ammonia would decrease titratable acidity and increase Brix/acid ratio used in part to judge fruit maturity. However, the information on degree of penetration of ammonia is worthy of note.

Table 1. Decrease in juice acidity by treating oranges with 10 percent NH_3 in 0_2 at 100°F.

Treatment	Time	pH	Titratable acidity	Total citrate [1]
	HR.		Percent citric acid	mM
Air	16	3.52	1.35	14.3
10 percent NH_3 in 0_2	16	3.52	1.32	13.8
Air	40	3.55	1.26	12.7
10 percent NH_3 in 0_2	40	5.00	.75	10.2

[1] Citrate determined enzymically.

ANALYSIS OF VOLATILE CARBONYLS IN ORANGE JUICE AS RELATED TO STORAGE CONDITIONS

by

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U.S. Fruit and Vegetable Products Laboratory
Winter Haven, Fla.

(Presented by Howard L. Dinsmore)

The naturally pleasant flavor and aroma of orange juice deteriorate during prolonged storage at warm temperatures. Juice stored at 85°F. develops a very disagreeable odor when compared with the fresh aroma of juice stored at 40°. Gas chromatographic analysis of juice volatiles appears to be a particularly useful means for following concomitant chemical changes, which in turn could be related to underlying autoxidative and enzymatic processes.

Many techniques for studying juice volatiles have been explored and generally suffer one or more disadvantages. Methods of concentrating or trapping juice volatiles, that is, distillation, extraction, and freezing, all permit easy loss of very volatile components; however, the volatiles captured in this manner are readily subject to Gas Liquid Chromatograph (GLC) analysis. On the other hand, chemical trapping of volatiles is highly efficient but direct GLC analysis of these trapped derivatives is not always possible.

The present study was undertaken to investigate the possibility of coupling chemical trapping with direct GLC analysis. Our study has been limited to aldehydes and ketones and has the following salient features: (1) nitrogen stripping of volatiles at reduced pressure; (2) chemical trapping of carbonyls by dinitrophenylhydrazine (DNPH); (3) GLC analysis of regenerated free carbonyls; and (4) mass spectral verification of GLC peaks. By using an efficient carbonyl regeneration procedure, we have both the efficiency of chemical trapping and the simple directness of GLC analysis. Small sample size and a minimum of sample handling make the procedure convenient for observing chemical changes during storage. We have successfully tested it on a model juice which was spiked with known aldehydes in the parts-per-million (p.p.m.) range. Nitrogen-stripped, freshly reamed pineapple orange juice was used as the model juice. Commercially prepared single-strength juice in glass containers was sampled after 20 months' storage at 40° and 85°F.

The flow diagram of figure 1 describes the stripping and trapping procedures. Volatiles were stripped from about 500 ml. of juice by a stream of nitrogen under partial vacuum and were passed directly into an alcohol solution of DNPH reagent. Dinitrophenylhydrazines which precipitated directly from the cold reagent were filtered; those still in solution were extracted by ethyl acetate, which was later evaporated. The entire carbonyl content thereby ended up in just two DNPH products; namely, an initial precipitate and a final residue. Direct regeneration of these into the gas chromatograph, as outlined by Jones and Monroe [1] completed the carbonyl analysis. Infrared spectra and thin-layer chromatograms of the DNPH fractions assisted in their characterization. Through the combined use of these methods and particularly the direct MS identification of GLC peaks, positive identifications have been made.

We have found a distincitive difference between fresh and aged juices during stripping and chemical trapping; namely, the initial precipitate from fresh juice or from juice stored at 40°F. shows the yellow DNPH of acetaldehyde, whereas the initial precipitate from juice stored at 85° is the red DNPH of furfural. The latter juice shows no acetaldehyde, a surprising find when one considers its prominence before storage.

The remaining DNPH fractions from all juices were similar in containing butanone, n-butyraldehyde, and acetone in decreasing abundance. The prominence of C_4 carbonyls was an unexpected result. No significant amount of C_6 and higher carbonyls was observed. Since identical experiments on model juices were entirely successful in volatilizing and capturing carbonyls up to C_{10}, the near absence of these in the actual juices seems valid, at least for the comparatively small dilute aqueous samples of this study.

This procedure is now being adapted to studies on total volatiles and their changes during storage.

DISCUSSION

QUESTION: How much material is required for analysis?

DR. DINSMORE: As much material as required for a capillary melting point. One can make about four or five GLC runs from the amount of material trapped out of one stripping experiment. There is also enough material for IR analysis as well.

QUESTION: How quantitative is this method?

DR. DINSMORE: The procedure was not tested for quantitation. We were more interested in the qualitative identification of components. However, in the model juice experiment, the GLC peak heights of the different carbonyls were essentially similar when equivalent amounts were added. It appears that there was no loss of carbonyl even though the volatility of the carbonyls differed considerably.

QUESTION: How efficient is the stripping technique?

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[1] Jones, L. A., and Monroe, R. J. Flash Exchange Method for Quantitative Gas Chromatographic Analysis of Aliphatic Carbonyls from Their 2,4-Dinitrophenylhydrazones. Anal. Chem. 37: 935-938. 1965.

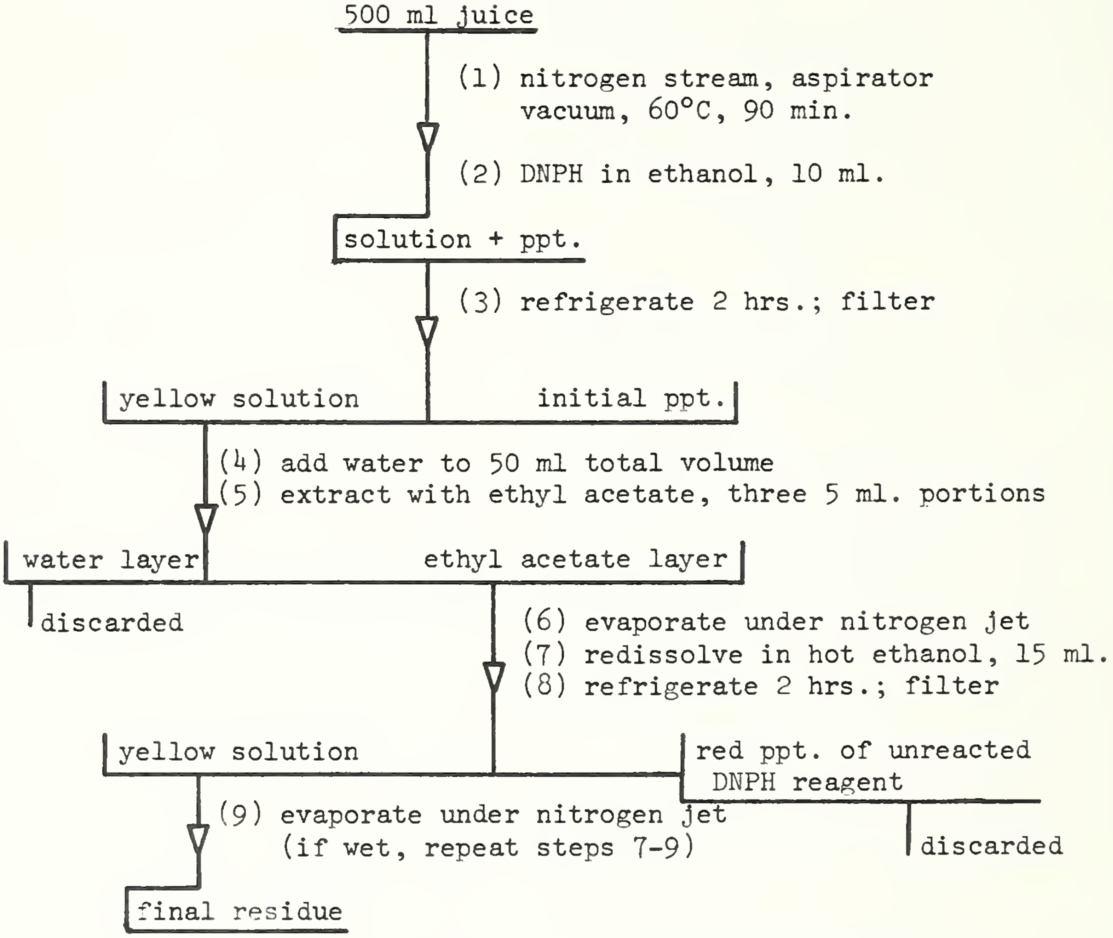
500 ml juice
(1) nitrogen stream, aspirator vacuum, 60°C, 90 min.
(2) DNPH in ethanol, 10 ml.
solution + ppt.
(3) refrigerate 2 hrs.; filter
yellow solution
initial ppt.
(4) add water to 50 ml total volume
(5) extract with ethyl acetate, three 5 ml. portions
water layer
ethyl acetate layer
discarded
(6) evaporate under nitrogen jet
(7) redissolve in hot ethanol, 15 ml.
(8) refrigerate 2 hrs.; filter
yellow solution
red ppt. of unreacted DNPH reagent
(9) evaporate under nitrogen jet (if wet, repeat steps 7-9)
discarded
final residue

Figure 1. Flow chart of stripping and subsequent operations.

DR. DINSMORE: The juice used in the spiking experiments show that there is some residual carbonyl remaining after stripping; however, these were found to be present at very low concentrations. We, therefore, concluded that the stripping technique is quite efficient.

QUESTION: With this technique, was it possible to assess the quality of a juice?

DR. DINSMORE: As of this date, employing this technique to assess the quality of a juice has not been made. We are simply presenting a technique for the determination of carbonyls in orange juice. This technique has not been used to determine off-flavor carbonyl compounds; however, this technique can be employed for this type of investigation.

QUESTION: How does this technique compare with other techniques for detecting small quantities of carbonyls in juice? Isn't it a fact that other techniques have a borderline of detection in the p.p.m. region?

DR. DINSMORE: Yes, with this technique we can detect carbonyls in the p.p.m. region. The limits of detection is vastly superior to other established methods.

QUESTION: Wasn't the 85°F. stored juice pretty bad for test tasting and wouldn't the presence of furfural and related compounds indicate storage abuse?

DR. DINSMORE: The 85°F. stored juice was not used for tasting as the odor was extremely offensive. One may observe that the content of furfural and related compounds increased under these extreme conditions. However, this increase may not have any direct relationship with the source of the terrible odor.

QUESTION: There are a number of products found in the browning reaction in meat with furfural-like properties. Have you checked out these furfural-type compounds in stored orange juice?

DR. DINSMORE: We have not investigated this type compound but we wondered about some peaks found past furfural which possessed furfural-like cracking patterns in the M.S. We will in the future look more closely at these compounds.

ANALYSIS, BIOCHEMISTRY, AND JUICE TECHNOLOGY OF LIMONOID BITTER PRINCIPLES OF CITRUS FRUITS

by

Vincent P. Maier, Shin Hasegawa, Linda C. Brewster,
and Dale Ryan
Western Marketing and Nutrition Research Division
Fruit and Vegetable Chemistry Laboratory
Pasadena, Calif.

(Presented by Vincent P. Maier)

In recent years we have been studying the biochemistry of limonin in an effort to help solve the problem of delayed bitterness in citrus juices. At the 1968 Conference on Citrus Chemistry and Utilization, I presented the results of our research on the mechanism of delayed bitterness. We found that the intensely bitter compound limonin does not occur in significant amounts in the edible tissues of intact citrus fruits. Instead, a nonbitter precursor of limonin, limonoate A-ring lactone is found (2,7). It occurs in the structural tissues of the endocarp and in the peel of the fruit. Limonoate A-ring lactone is readily converted into limonin in solutions having the same acidity as citrus juices. Therefore, in juice manufacture when the broken tissues of the fruit mix with the acidic juice, the non-bitter limonoate A-ring lactone, which is unstable under these conditions, is converted to the bitter compound limonin and the juice becomes bitter. If the juice is heated, the rate of conversion of the nonbitter precursor to limonin is increased and the juice becomes bitter more rapidly. However, only those fruits which contain significant amounts of limonoate A-ring when mature produce bitter juices.

During work on the identification of the limonoate A-ring lactone a new enzyme was discovered in citrus fruit tissue extracts which catalyzes the conversion of limonoate A-ring lactone to limonin in acidic solutions such as citrus juices (6). However, in neutral to alkaline solutions such as the cytoplasm of cells, the enzyme (which was named limonin D-ring-lactone hydrolase) catalyzes the hydrolysis of limonin to limonoate A-ring lactone. This enzyme appears to be the missing link needed to account for the presence of limonoate A-ring lactone and the absence of limonin in the tissues of intact citrus fruits — that is, the absence of bitterness of the fresh navel orange as contrasted with the bitterness of its juice.

Further studies on the biochemistry and juice technology of limonoids required the development of a specific and sensitive quantitative method for determining limonin in all types of citrus tissues and juices. Such a method has been developed by combining the ability of thin-layer chromatography (TLC) to separate limonin from other citrus constituents (3) and the selectivity and sensitivity of Ehrlich's reagent for limonoids (1) with the general extraction procedures of Wilson and Crutchfield (8). In this TLC assay (4), limonin, once it is formed in citrus juices, is removed by two extractions with chloroform; the chloroform extracts are combined and evaporated; and the residue is dissolved in a measured volume of acetonitrile. The acetonitrile soltuion is quantitatively spotted on a silica gel thin-layer chromatogiam along with authentic limonin; the chromatogram is developed in benzene: ethanol: water: acetic acid (200:47:15-1, upper phase), dried, sprayed with Ehrlich's reagent, and treated with gaseous HCl. Readout is by visual or spectrodensitometric comparison of the unknown and known limonin spot densities.

Reproducibility of the method was tested with samples of lemon, orange, and grapefruit juices and their concentrates; it was routinely ±5 percent and better. Recoveries of known amounts of limonin added to citrus juices were quantitative over the range 0.5 to 500 p.p.m. On a routine basis it was possible to determine limonin contents as low as 0.5 p.p.m. with 20-gram samples of juice. Lower limonin concentrations have been determined by using larger samples.

In addition to its use in determining the limonin content of citrus juices, the TLC assay can also be used to determine indirectly the limonate A-ring lactone (or potential limonin) content of fruit tissues after extraction and acid conversion of this nonbitter precursor to limonin. With the approach, Maier, Grant, and Hasegawa (5) found that in a yellow-ripe lemon the various tissues of the fruit contained the following percentages of total potential limonin: peel, 74.0 percent; section membranes, 20.2 percent; juice sac walls, 3.3 percent; and cheesecloth filtered juice, 2.5 percent. This juice, prepared directly from the carefully separated juice sacs by pressing on cheesecloth with suction removal of the juice, contained 8 p.p.m. limonin. Thus, even when the juice is prepared in a very gentle manner, a significant amount of limonoate A-ring lactone enters the juice and is converted into limonin. If all of the limonoate A-ring lactone contained in the juice sac walls had entered the juice, the limonin content would have been 18 p.p.m., and the juice would have been extremely bitter. If, in addition, small percentages of the limonoate A-ring lactone of the section membranes and peel had entered the juice, its limonin content would have been considerably higher. These figures point out the extreme importance of gentle juice extraction procedures and short contact time between juice and pulp to minimize limonin bitterness in the juice.

It has been observed over the years that navel oranges harvested up to several months after becoming ripe (early- to mid-season fruit) produce juice that undergoes delayed bitterness whereas fruit harvested several months later (late-season fruit) produce nonbitter juice. Subsequently Maier and Beverly (2) and Maier and Margileth (7) showed that navel oranges that produce bitter juice contain limonoate A-ring lactone in the endocarp tissues while those that produce nonbitter juice do not contain that compound. Thus, as navel oranges approach late-season maturity limonoate A-ring lactone gradually disappears from the fruit tissue. This observation is important because it shows that the limonoate A-ring lactone content of the fruit is in a dynamic state, and that native enzymes are capable of metabolizing it to nonbitter products which remain nonbitter even when the fruit is converted into juice. It has also been shown (Maier, unpublished) that whereas the tissues of immature Valencia oranges contain limonoate A-ring lactone, the compound could not be detected in the tissues of mature early-season Valencia oranges. Thus, it appears that the enzyme system that metabolizes limonoate A-ring lactone has sufficient time to act to result in nonbitter juice before Valencia oranges reach commercial maturity. With navel oranges this is generally not the case. Time is required after commercial maturity is reached for the enzyme system to metabolize sufficient limonoate A-ring lactone to result in nonbitter juice. Based on the presence of significant amounts of limonin in the juices extracted from commercially mature grapefruit and lemons, these species resemble the navel orange with regard to the activity of this enzyme system.

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DISCUSSION

QUESTION: Do you have any data on what influence weather or agriculture has on the limonin content?

DR. MAIER: Any of those practices that have an influence on the rate of maturation of the fruit would influence the limonin content. We do not have any specific data. However, we have observed that in a cold year, when the fruit wasn't ripening as rapidly as expected, a higher limonin content was observed than that observed at the same time during a normal year.

QUESTION: Is lycopene formed in the juice or mostly in the peel?

DR. MAIER: Lycopene is formed in any tissue that comes in contact with the chemical. Of course, you have to have penetration of the chemical into the interior if you are to get lycopene accumulation there. In these experiments these sites were primarily the flavedo and the albedo.

QUESTION: What material do you use?

DR. MAIER: It is called CPTA, 2-(4-chlorophenylthio)-triethylamine. It has not been approved for use on foods.

QUESTION: Is there much residue left on the fruit?

DR. MAIER: We have not studied that aspect at this time. Our research is still in the preliminary stages. We are interested in finding out how it works, etc. There may be potential applications here with the Ruby grapefruit, tomatoes, etc. One can cause this coloring at various stages of the maturation process. It would have to be cleared by Food and Drug for food use, however.

QUESTION: How is the chemical applied to the fruit and how long does it take to color the fruit?

DR. MAIER: In the last slide, Marsh grapefruit is shown 13 days after application of the chemical. (Fruit were quite red in color.) We did not spray the entire tree but dipped the individual fruit. There isn't that much compound around.

QUESTION: Was that Marsh white grapefruit?

DR. MAIER: Yes, it was. It would work on the Ruby also. We chose the Marsh to show the magnitude of the effect.

QUESTION: Are there changes in the other pigments?

DR. MAIER: Depending on the maturity of the fruit, it does not affect those carotenoids which have already been laid down but simply overlays with lycopene. If you applied it to a position where there had not been too much carotenoid deposition, then you would be going mostly into lycopene. If you applied it after there were numerous carotenoids present, you would have these carotenoids plus the new lycopene formed. This, then, is a stimulation of carotenoid synthesis.

QUESTION: Does the fruit have to be on the tree for this to take place?

DR. MAIER: No, it doesn't. The last slide shows post-harvest treatment of Marsh grapefruit.

QUESTION: How long does the fruit stay red and is there any damage to the fruit?

DR. MAIER: We have not done any long-term experiments; however, as long as the fruit remains healthy looking the effect is still there. The last slide shows the fruit still healthy 13 days after the color had formed. If you use high levels, you get peel damage but at the lower levels the damage is minimum. Before you reach full color, the fruit is a bit blotchy but the color voids fill in as time goes by.

QUESTION: Concerning the limonin studies, have you any storage study data on the length of time this compound stays in the fruit? Does the content decline?

DR. MAIER: Yes, there is a gradual decline. In our studies with lemons, we found the half life — that is the time for one-half the limonin to disappear — to be 6 weeks at 58°F.

QUESTION: Is there a relationship between rootstock and limonin content?

DR. MAIER: Yes, there has been a lot of work done on this in past years by Dr. Chandler in Australia and Dr. Marsh at Davis, Calif. For example, the sour orange is not a good rootstock, however, the sweet orange is. In fact, Dr. Chandler reported that some seedling sweet oranges in Australia were quite good. Grapefruit stock for orange on the other hand is fair to poor.

QUESTION: Did you taste the juice of the fruit where lycopene color was induced?

DR. MAIER: We have not. These were preliminary studies. This will have to be done if the use is to be commercialized. We are studying now other compounds — analogs of this compound and other types of compounds — to see whether there are simpler compounds which will do the same thing.

QUESTION: Concerning this compound (CPTA), is it available now commercially?

DR. MAIER: It is not made in large amounts. The material is an experimental compound prepared by Amchem and I believe it could be obtained from them.

GRAPEFRUIT ESSENCE CONSTITUENTS

by

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U. S. Fruit and Vegetable Products Laboratory
Winter Haven, Fla.

(Presented by Manuel G. Moshonas)

The term "essence" is commonly used by the citrus industry to describe the aqueous solution which is recovered during the process of concentrating fresh juice. Essence is rich in volatile flavor components and has a pleasant aroma characteristic of the fresh fruit from which it comes.

Grapefruit essence currently can be collected in commercial essence recovery units, but to date has not been widely used to enhance the flavor and aroma of grapefruit products. However, the consumer acceptance of orange essence, which is widely used to improve flavor of orange products, and the availability of grapefruit essence indicate the need for information on the flavor constituents in grapefruit essence.

The only previous investigation of volatile grapefruit juice constituents was reported by Kirchner and coworkers.[1][2] The water soluble grapefruit components they reported were acetaldehyde, methanol, and ethanol. Juice oil constituents reported which were also found in our investigation were limonene, carvone, linalool, α-terpineol, and 3-hexen-1-ol.

In our investigation, 32 volatile flavor compounds were identified as aqueous grapefruit essence constituents after extraction with ethyl ether and methylene chloride and separation of the extracted components with gas chromatography. Figure 1 shows the gas chromatogram of the methylene chloride extract on Carbowax 20M. Acetal, methanol, and ethanol were separated and identified from the ether extract. The six most volatile components were positively identified by mass spectrometry and retention times while the remaining 26 components were identified by mass spectrometry, infrared spectroscopy, and retention times.

The eight previously reported compounds were all found along with the following 24 compounds being reported as grapefruit juice constituents for the first time: acetone, ethyl acetate, acetal, methyl butyrate, ethyl butyrate, isobutyl alcohol, hexanal, butyl alcohol, isoamyl alcohol, 2-hexenal, octanal, hexanol, trans-linalool oxide, cis-linalool oxide, octanol, terpinen-4-ol, trans-2, 8-p-menthadien-1-ol, ethyl 3-hydroxyhexanoate, neral, geranial, trans-carveol, cis-carveol, 8-p-menthene-1, 2-diol, and nootkatone.

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[1] Kirchner, J. G., and Miller, J. M. Volatile Oil Constituents of Grapefruit Juice. J. Agr. Food Chem. 7: 512-518. 1953.

[2] Kirchner, J. G., Miller, J. M., Rice, R. G., and others. Volatile Water-Soluble Constituents of Grapefruit Juice. J. Agr. Food Chem. 7: 510-512. 1953.

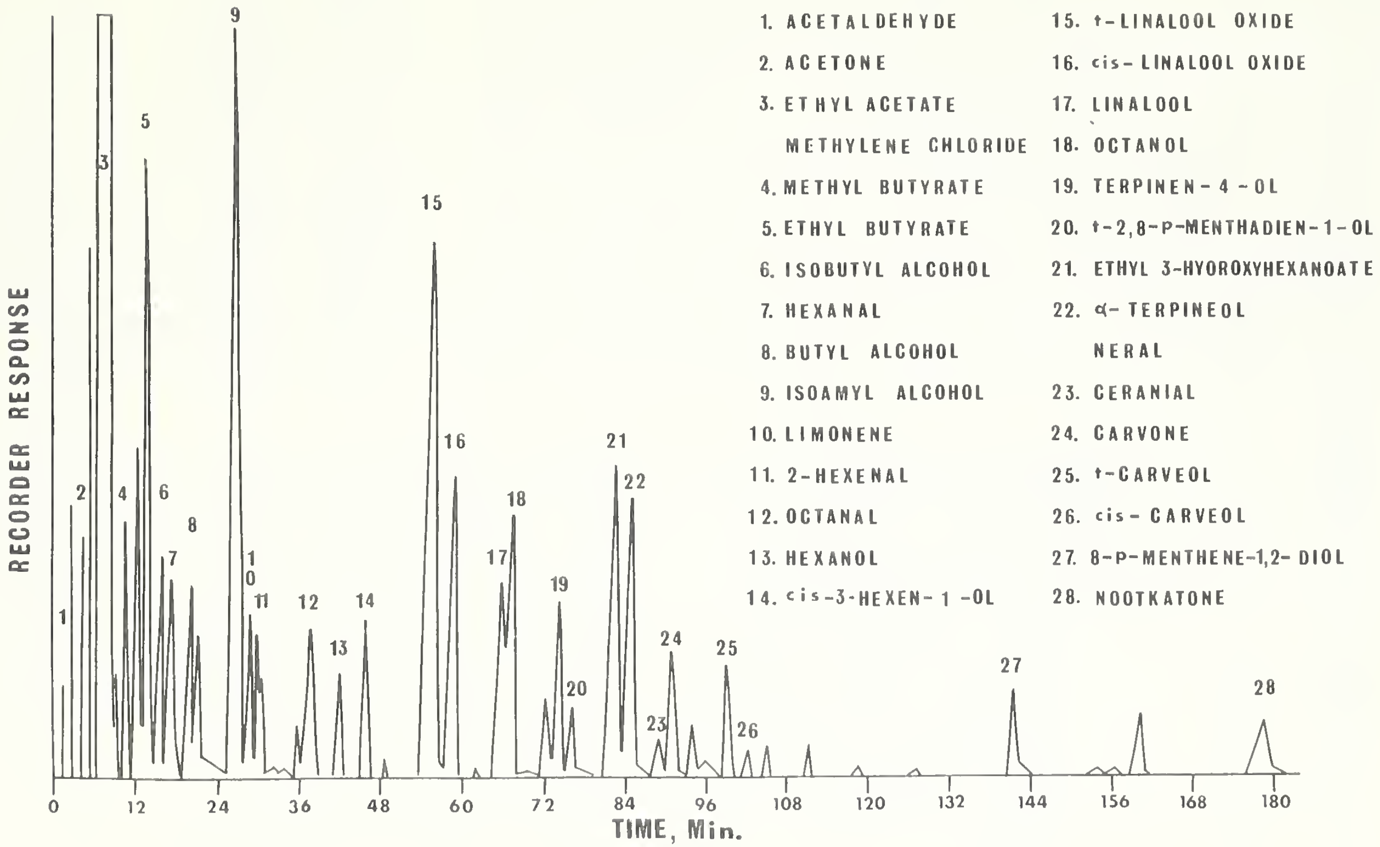

Figure 1. Gas chromatogram of nonaqueous grapefruit essence.

ANALYSIS OF VALENCIA AROMA AND ESSENCE OILS

by

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Southern Marketing and Nutrition Research Division
U. S. Fruit and Vegetable Products Laboratory
Winter Haven, Fla.

(Presented by Philip E. Shaw)

Orange essence oil is part of the volatile fraction condensed directly from orange juice by commercial essence recovery units during the process of concentrating the juice. Essence oil is separated from the aqueous layer before aqueous essence is collected (1, 3, 6). This essence oil is currently a byproduct in aqueous essence production, but its essence-like odor quality, its colorless appearance, and its increasing availability make this oil a useful flavoring agent.

Distilled aroma oils and aqueous aroma solutions have been produced in our laboratories using, as feedstock, the aqueous discharge from Valencia orange peel oil centrifuges (5). These aroma oils are similar to essence oils both in odor and physical appearance and should be good flavoring agents for orange products. Since little is known about the composition of these aroma oils, an analytical study was undertaken. This paper reports the results of that study.

Four distilled Valencia orange oils were studied. Two of these were essence oil samples obtained commercially. Sample No. 1 came from the same source as the oils described previously (2) and sample No. 2 from a source using an essence recovery unit of different design from that of the first. The remaining two oils were aroma oils (samples Nos. 1 and 2) prepared from centrifuge effluent as previously described (5). All samples were stored at 40°F. until analyzed. Each of the four oils were analyzed by gas liquid chromatograph (GLC). This method of direct injection of whole oils is referred to as "whole oil" analysis.

Main components identified from the essence and aroma oil samples examined by whole oil analysis are listed in table 1 in order of their GLC retention times. Spectral means of identifying each component and quantitative estimates are also given. A quantitative estimate is listed for each compound identified by rt and spectral data. When no quantitative value is listed, the compound was present in quantity too small to be trapped. The one exception was myrcene which appeared as a shoulder on the D-limonene peak and could not be estimated quantitatively. These oils were amenable to GLC analysis as received, because they had each been distilled during their preparation. Thus, the carotenoids, waxes, and other higher boiling components that make GLC analysis of cold-pressed oils difficult had already been separated from these distilled oils in their preparation.

The essence and aroma oils were similar in composition, both by qualitative and by quantitative estimation. A major quantitative difference was the relatively high percentage of Valencene (0.5 percent) found in the two essence oil samples, while the aroma oils both had less than 0.1 percent Valencene. Amounts of carvone and trans-carveol were less than 0.1 percent except for aroma oil sample No. 1, which had 0.34 percent carvone and 0.22 percent trans-carveol. This latter aroma oil sample had been stored for 1 year at 40°F. prior to whole oil analysis whereas the other three oil samples listed in table 1 were all analyzed within a month after their preparation (which may account for this observation). Carvone and trans-carveol amounts should increase in these oils during storage, since orange peel oil shows increased amounts of carvone and carveol after storage (4). One essence oil and one aroma oil sample were each separated, using a Swissco evaporator, into three fractions for further study. Essence oil No. 1 (500 ml., 420 ± 2 g.) was distilled at 31°C. under 0.9-mm. pressure to

Table 1.--Quantitative essence and aroma oil composition

			Percent area under curve			
		Spectra	Aroma oil		Essence oil	
Compound	rt(min.)[1]	obtained	No. 1[2]	No. 2	No. 1	No. 2
α-Pinene	12	ir	0.30	0.45	0.30	0.16
Myrcene	16	ir				
D-Limonene[3]	22.5	ir	96.0	96.4	96.0	97.4
Octanal	23.5	ir, ms	.55	.44	.89	.47
Nonanal	26.5	ir, ms	<.1	<.1	.1	<.1
Decanal	29.5	ir, ms	.43	.65	.70	.47
Linalool	30	ir, ms	.63	1.14	.62	.54
α-Terpineol	37.5	ir	.14	.15	<.1	<.1
Geranial	39	ir, ms	.12	.1	.15	.1
Carvone	40	ir, ms	.34	<.1	<.1	<.1
Valencene	40.5	ir, ms	<.1	<.1	.5	.54
Perillaldehyde	42.5	ir, ms	<.1	<.1	<.1	<.1
Trans-Carveol	43	ir	.22	– –	– –	– –
Cis-Carveol	44	ir	.12	– –	– –	– –
1, 8-p-Menthadien-9-o1	48.5	ir	.1	– –	– –	– –

[1] Carbowax 20M column.

[2] Stored 1 year at 40°F.

[3] $[\underline{\alpha}]_{D}^{29^\circ}$ + 117° ($\underline{c}$ 1.15 in EtOH).

give 13.9-g. pot residue, 402 g. chilled water condensate (mostly D-limonene), and 5.0-g. liquid nitrogen trap condensate. Portions of these fractions were recombined for the odor panels discussed below. Aroma oil No. 1 (820 g.) distilled at 2.5 to 1.0 mm. with a bath temperature of 45° C. maximum yielded 19.5-g. pot residue, 799-g. chilled water condensate (mostly D-limonene), and 1.2-g. liquid nitrogen trap condensate. Both the pot residue and chilled water condensate from this aroma oil were separated into several fractions by liquid chromatography on Florisil and each fraction was analyzed by GLC.

Table 2 is a composite list of the 42 components identified in aroma oil sample No. 1. It includes results from GLC analysis of all liquid chromatography fractions as well as the liquid nitrogen trap condensate. The compounds are listed by functional group classes in order of their retention times on a polar column. Listing of an additional rt on a nonpolar (UCW-98) column indicates that the sample had to be collected from a polar column and rechromatographed on a nonpolar column to be adequately purified.

This aroma oil is qualitatively similar to midseason and Valencia essence oils reported earlier from this laboratory (2). Quantitative estimation of minor components isolated by liquid column chromatography was not made because of the likelihood of error due to (1) losses of material on the column, and (2) required corrections for large solvent peaks still present after individual fractions were concentrated to small volume and analyzed by GLC. Quantitative estimates for main components as given in table 1 are more meaningful, since introduction of solvents and liquid column chromatography were avoided. More components were found in aroma oil than had been found previously in essence oil. This is primarily due to the analysis of liquid nitrogen trap condensate, a fraction not previously examined from essence oil.

Table 2.--Qualitative aroma oil composition

Compound	Spectra obtained	R.T.	
		20M	UCW-98
Acetals:			
Diethylacetal (acetal)	ms	16	4
Alcohols:			
Ethanol	ms	18	— —
Linalool	ir	44	— —
Octanol	ir,ms	46	— —
Nonanol	ir	51	— —
trans-2, 8-Menthadien-1-o1	ir	52	— —
Cis-2, 8-p-Menthadien-1-o1	ir	54	— —
α-Terpineol	ir, ms	56	41
Citronellol	ir, ms	56	— —
trans-Carveol	ir	64	— —
cis-Carveol	ir	66	— —
1, 8-p-Menthadien-9-o1	ir	74	— —
8-p-Menthene-1, 2-diol	ir, ms	90	— —
Aldehydes:			
Hexanal	ms	25	— —
Heptanal	ir	29	— —
Octanal	ir, ms	34	24
Nonanal	ir, ms	39	28
Decanal	ir, ms	46	— —
Neral	ir, ms	56	43
Geranial	ir, ms	59	44
Dodecanal	ir, ms	61	52
Perillaldehyde	ir	63	— —
Esters:			
Ethyl butyrate	ms	25	7
1, 8-p-Menthadien-9-o1 acetate	ir	66	— —
Hydrocarbons:			
Hexane	ms	3	— —
Isoprene	ir, ms	4	— —
Methylcyclopentane[1]	ms	5	— —
Heptane[2]	ms	5	— —
Octane	ms	10	— —
Nonane	ir, ms	15	— —
α-Pinene	ir, ms	25	— —
Sabinene	ir	31	— —
Myrcene	ir	33	— —
D-Limonene	ir	38	— —
β-Cubebene	ir, ms	50	— —
β-Elemene	ir	53	48
β-Copaene	ir	55	— —
Valencene	ir, ms	61	— —

Table 2.--Qualitative aroma oil composition (Cont)

Compound	Spectra obtained	R.T. 20M	R.T. UCW-98
Ketones:			
Actone	ir, ms	10	— —
Ethyl vinyl ketone	ms	24	— —
Carvone	ir, ms	61	43.5
Pipertenone	ir, ms	71	48

[1] Front half of GLC peak.
[2] Back half of GLC peak.

Volatiles identified in the liquid nitrogen trap condensate from both aroma oil No. 1 and essence oil No. 1 are listed in table 3. In each case, this fraction was judged to possess most of the essencelike odor characteristic of essence and aroma oils, and was therefore worthy of careful examination. Three of the compounds found in these fractions not previously reported in citrus are: ethyl vinyl ketone, isoprene, and ethyl propionate.

An odor panel judged the liquid nitrogen trap condensate separated from essence oil No. 1 to be necessary for the original oil to have a full essence-like odor. The panel judged an oil reconstituted from pot residue and chilled water condensate (omitting liquid nitrogen trap condensate) to have less essencelike odor than the original oil. A reconstituted oil that included the proper proportion of liquid nitrogen trap condensate was judged to have more essencelike

Table 3. Volatiles from essence and aroma oils

Compound	Found in — —		rt(min.)[1]	
	Essence oil	Aroma oil	20M	UCW-98
Acetaldehyde	X	— —	— —	2
Hexane	—	X	— —	— —
Isoprene	—	X	— —	— —
Heptane	X	X	3	12
Methyl cyclopentane	—	X	— —	— —
Acetone	X	X	6	— —
Ethyl acetate	X	— —	8	7
Acetal	—	X	— —	— —
Ethanol	X	X	10	3
Ethyl propionate	X	— —	13	12
Methyl butyrate	X	— —	16	13
Ethyl vinyl ketone	X	X	20	10
Ethyl butyrate	X	X	24	22
α-Pinene	X	X	24	— —
Hexanal	—	X	— —	— —
Myrcene	X	X	47	— —
D-Limonene	X	X	58	— —
Octanal	X	X	60	— —

[1] When isolated from essence oil.

odor than the original oil. Both judgments were at the 95 percent confidence level (10 correct judgments out of 12 presentations). Thus, the most volatile components in essence oil are important contributors to essencelike odor of the oil.

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DISCUSSION

QUESTION: Was the original paper on essence oils from your laboratory in error in not reporting aldehydes as being present?

DR. SHAW: The aldehydes were probably present in the oils analyzed earlier and were believed to be lost during the liquid column chromatography step, although we cannot be sure.

QUESTION: Could the lack of acetaldehyde in essence oil volatiles be due to loss during the distillation step?

DR. SHAW: I do not think so, because the aroma and essence oil samples were both distilled under identical procedures, and acetaldehyde was found in the aroma oil volatiles.

COMPARATIVE QUANTITATIVE ANALYSES OF ORANGE PEEL AROMA SOLUTIONS

by

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and Charles J. Wagner, Jr.
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(Presented by Eric D. Lund)

A method has been developed for the quantitative composition analysis of aqueous essences. This new approach involves use of one GLC procedure to determine the three major components, followed by solvent extraction and combined GLC/Mass spectrometric analysis to determine the other principal constituents.

At the 1968 Conference, the composition of aqueous essences obtained from various parts of the orange fruit and from peel oil desludger effluent was reported.[1] In that study the solvent extraction method of Wolford and others [2] was used to obtain an anhydrous sample suitable for GLC analysis. The aroma solutions from centrifuge effluent, along with the other essences derived from different parts of the peel, were found, by that analysis, to contain most of the compounds reported in commercial juice essence.

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[1] Veldhuis, M. K., Berry, R. E., Wagner, C. J., Jr., and Moshonas, M. G. Studies on Recovery of Water Soluble Essences and Distilled Oil from Orange Peel. 1968 Conf. Citrus Chem. Util.Proc., U. S. Dept. Agr., Agr. Res. Serv. ARS 72-73: 18-19. 1969.

[2] Wolford, R. W., Alberding, G. E., and Attaway, J. A. Analysis of Recovered Natural Orange Essence by Gas Chromatography. J. Agr. Food Chem. 10: 297-301. 1962.

Since that time, much of the work on aroma solutions from peel has centered around the use of centrifuge effluent as a source. Information was needed on how the variables in the essence affected amounts of the constituents. To this end, a method was developed to determine the percentage composition of a number of the peel essence products derived from centrifuge effluent using GLC analysis with a flame ionization detector.

Methanol, acetaldehyde, and ethanol accounted for the bulk of the organic material in these essence products. A column of Porapak, a hydrophobic, porous polymer packing, was used in order to allow a GLC analysis for these three compounds without interference from a broad, highly tailed water peak.

In figure 1, a typical GLC trace is shown, illustrating the relative order of elution of water methanol, acetaldehyde, and ethanol from the Porapak column. There are no peaks discernible from the baseline at longer retention times because of the relatively small amount of the other constituents.

The remainder of the essence components were analyzed by the previously used solvent extraction method involving saturation of the aqueous essence with sodium sulfate and extraction with methylene chloride. GLC traces were obtained from the concentrated methylene chloride extract on two different polar columns, Carbowax 20M and DEGS,[3] and on a nonpolar column, SE-30. By a combination of mass and infrared spectrometry and retention times, 43 compounds were isolated from the essence. A quantitative analysis was obtained for 14 of these, which accounted for over 90 percent of the material appearing in the GLC traces. Table 1 lists the 14 compounds along with methanol, acetaldehyde, and ethanol and the range of concentrations observed. Linalool, limonene,

Table 1. Peel essence constituents

Compound	Concentration range		
	Wt.	pct.	x 10^3
Methanol	41	to	820
Acetaldehyde	4	to	68
Ethanol	25	to	640
Linalool	1.5	to	4.6
Limonene	.26	to	2.3
α-Terpineol	.18	to	1.7
Cis-3-hexene-1-o1	.33	to	2.5
n-Octanal	.17	to	.65
l-Octanol	.14	to	.74
l-Hexanol	.15	to	1.18
n-Hexanal	.13	to	.51
n-Amyl alcohol	.056	to	.56
t-2-Hexanal	.12	to	.84
t-Linalool oxide	.014	to	.076
Geranial	.012	to	.227
Terpinene-4-o1	.028	to	.194
Neral	.24	to	— —

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[3] See footnote 2, page 15.

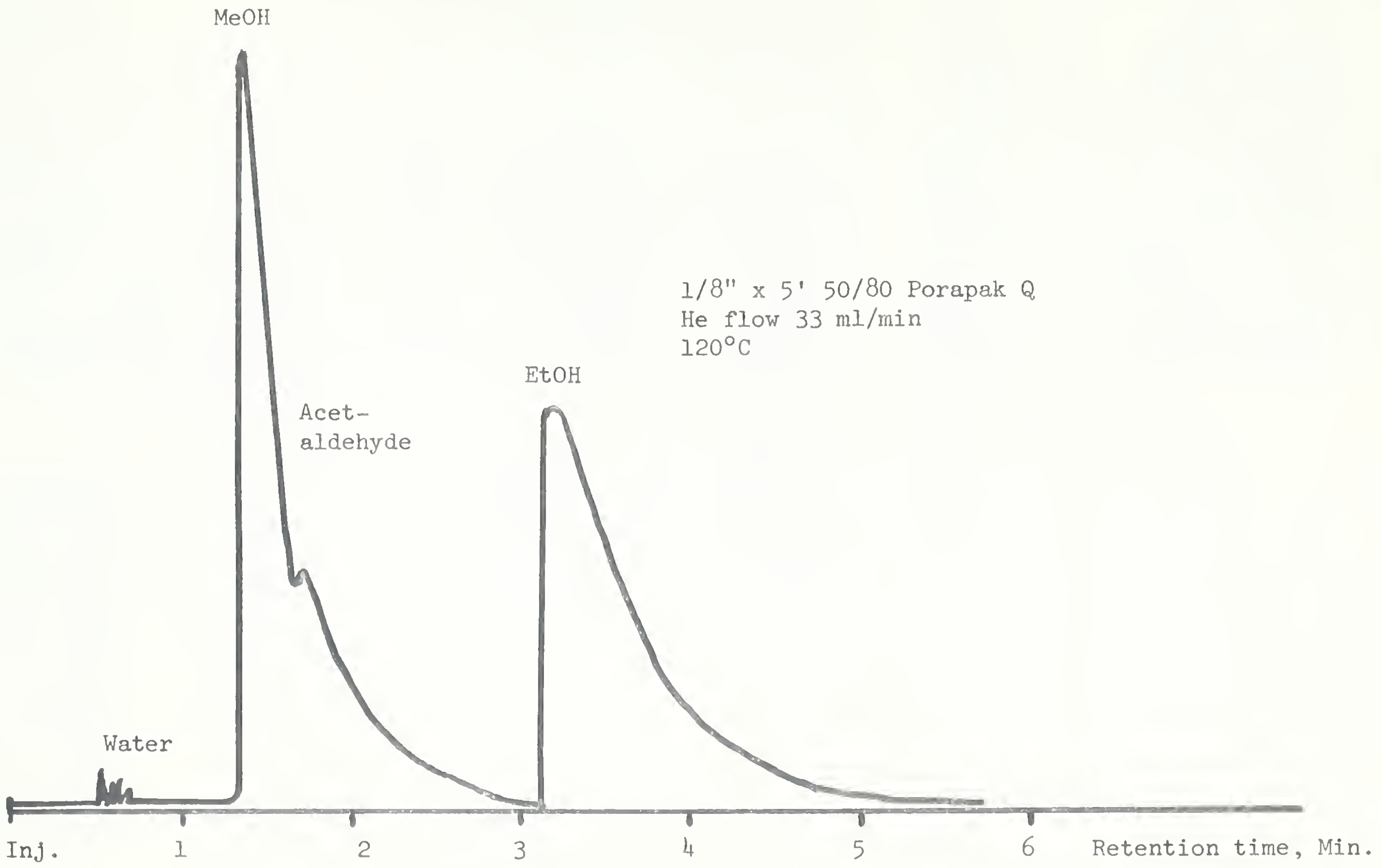

Figure 1. GLC trace of aqueous essence on Porapak.

α-teripineol, and cis-3-hexene-1-o1 were the major components in the higher boiling fraction. Because of the general similarity in composition, this method should be easily adapted for the analysis of juice essence as well.

DISCUSSION

QUESTION: Murdock and his group have shown that bacterial contamination has considerable influence on the amount of α-terpineol found in oil emulsions. Since you have been working with orange oil emulsions, would you have a completely sterile system with which you worked? Bacteria might also influence other alcoholic constituents.

DR. LUND: No, they are not sterile, of course. Bacterial contamination might be a factor, we haven't really checked into it. This is the centrifuge effluent that normally comes out of the plant which might contain extraneous material and we don't know the condition of these effluents with respect to bacterial contamination.

SESSION II: Kenneth W. Hastings, Chairman

USE OF REVERSE OSMOSIS PROCESS FOR CONCENTRATING CITRUS CENTRIFUGE EFFLUENT SOLIDS

by

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(Presented by Robert E. Berry)

Interest is increasing in methods of treatment for liquid wastes from food processing plants. One source of waste water from citrus processing plants is the aqueous discharge (effluent) from the peel oil mill. This effluent is usually discharged into sewage systems or settling ponds, and may contain 2 to 5 percent solids, 1 percent insoluble solids, and varying amounts of residual peel oil ranging up to 1 percent. Methods have been developed for stripping both oil and water-soluble volatiles from this effluent and are reported elsewhere. In order to provide a clean effluent for discharge into the sewer, methods were sought for the concentration of the remaining dissolved and suspended solids.

Due to its low operating cost in dilute ranges of concentration, reverse osmosis appeared the method of choice for concentration of desludger effluent. All of the work was carried out on units manufactured by Havens Industries, San Diego, Calif. Their eight-tube module of approximately 8 sq. ft. effective surface was used with membrane type 300 as specifically recommended for retention of molecules in the general size ranges of monosaccharides and disaccharides. Optimum feed rates of about 2 gal./min. at 600 p.s.i. maximum pressure were maintained. First experiments were carried out on grapefruit desludger effluent and included a study of the relationship between operating temperature and rate of concentration of solids. At the lowest temperature, around 40°F., it was not possible to reach 10° Brix at a reasonable rate. Rates slowed considerably as concentration increased and became extremely low beyond 6.5° Brix. The rate was 2.5 gal./ft.^{2}/day at 6.5° Brix. At 60°F., it was possible to achieve 10° Brix at a rate of about 3 gal./ft.^{2}/day. However, the highest rate was achieved at about 80°F. where 10.5° Brix was produced at almost 4 gal./ft.^{2}/day. Another run conducted at 100°F. almost coincided with the rate at 80°F. indicating little difference between those two temperatures and suggesting little advantage in proceeding to higher temperatures.

These data were also considered from the standpoint of the number of passes through an eight-tube (8 ft. ^{2} of membrane) module required to concentrate from about 2° Brix to about 10° Brix. This information might be of help in designing larger scaled operations. Feed material was passed through a module at the recommended rate of 2 gal./min. and the °Brix of feed and concentrate were compared. The concentrate was collected and passed through again and this process repeated until the desired Brix of about 10° was reached. Fewer passes were required, (that is, concentration increased at a greater rate) as temperature increased up to 80°F. At 40° F. the rate had slowed so much by the time 6.5° Brix was reached that concentration was not continued beyond that point. For the other temperatures studied, however, concentration to 10° Brix required 47 passes at 60°, 34 at 80°, and 36 at 100°F.

Following these studies orange effluent was concentrated at the optimum temperature 80°F. The curve of concentration rate vs. °Brix required approximately 39 passes as compared with the 34 required for grapefruit. An unexpected observation was made during this study. When concentration reached about 6° Brix, the rate began to fall off sharply. This was suspected to be due to an accumulation of oil or dissolved solids at the surfaces of the membrane. Therefore, a small amount of detergent solution was passed through at that point. The rate increased from about 3.75 gal./ft.^{2} /day to about 4.3 gal./ft.^{2} /day and again approximately coincided with the grapefruit data curve for this temperature. For this cleansing effect, a small amount of an acid detergent (Phisohex) solution which makes a pH 6.0 cleaning solution was passed through the module, timing it carefully in order to recover it after traversing the module.

DISCUSSION

QUESTION: Did you make any observations on the stability or life of the membrane?

DR. BERRY: No, we never had trouble with them up to 750 to 1,000 hours of use.

QUESTION: Was the liquid pasteurized first?

DR. BERRY: Yes.

QUESTION: What is the cost per square footage material?

DR. BERRY: I can't answer that. It will vary depending on the source and type. Manufacturers of equipment and membranes can give more information on this.

QUESTION: Did you run BOD, COD or bacterial check on the water effluent from your Reverse Osmosis treatment?

DR. BERRY: No. However, it looks, smells, and tastes like clean, distilled water. Material balance checks showed the water stream had negligible solids content.

REVIEW OF CITRUS RESEARCH AT THE WESLACO LABORATORY

by

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(Presented by B. J. Lime)

An investigation of the occurrence of the flavanone content of grapefruit at different stages of maturity has been continued. Previous reports indicate little change occurs in the relative amounts of the bitter form of the flavanones and the nonbitter forms during the various stages of mature fruit. Table 1 lists the relative flavanone content of grapefruit at different stages of development from the ovary to early maturity. The high percentage of the bitter naringenin neohesperiodoside was observed in the very early ovary state of fruit formation and continued at approximately the same relative level throughout fruit development.

The influence of the tree on flavanone composition of the fruit was demonstrated by grafting 3-cm. Redblush grapefruit onto five different citrus species, allowing the fruit to mature, and analyzing the juice for flavanones. With maturity, only minor expression of the flavanone synthesizing capacity of the bearing tree may be seen in the juice. When Redblush grapefruit budwood was grafted onto a mature sour orange tree, grapefruit was set and developed in the absence of any grapefruit leaves. Analyses of the fruit suggests that the genetic makeup of young developing grapefruit is the over-riding factor in determining the nature of the flavanones accumulated in the fruit.

In cooperation with Plant Science Research Division, ARS, USDA, an investigation was undertaken to relate changes in ethylene evolution and respiration of leaves exposed to subfreezing temperatures with abscission and severity of freeze conditions. Table 2 lists the extent of freeze damage, leaf abscission, and ethylene evolution from the leaves of pineapple oranges exposed to three freezing temperatures. The rate of ethylene evolution from freeze-damaged tissue indicates the extent of freeze damage to the tissue. Citrus leaves exposed to low temperatures with only a small amount of permanent injury induced ethylene evolution, while exposure to severe freeze temperatures which caused extensive leaf injury resulted in reduced ethylene evolution.

Efforts have been underway for several years at the Food Crops Utilization Research Laboratory, Weslaco, Tex., to improve the quality of natural flavored citrus bases and drinks. One of the projects now in progress is the production and utilization of whole citrus purees for drinks, drink bases, and powders. Whole citrus fruit puree, representing from 85 to 90 percent of the whole fruit was prepared after washing field-run fruit by the following six-step process: (1) blanching at 212°F. for 10 minutes; (2) coarse grinding through 0.5-inch screen; (3) finishing with rejection of seeds, some rag, and tough

Table 1. Relative flavanone content of grapefruit at different stages of development

	March '67 Ovaries	June '67 Whole fruit	November '66 Whole fruit
	Pct.	Pct.	Pct.
Naringenin neohesperidoside	75.8	77.7	75.3
Naringenin rutinoside	13.9	12.9	17.6
Hesperetin neohesperidoside	6.5	1.8	1.8
Hesperetin rutinoside	Tr	1.7	1.7
Isosakuranetin neohesperidoside	2.3	4.8	2.8
Isosakuranetin rutinoside	1.5	1.1	.8
	100.0	100.0	100.0

Table 2. Ethylene evolution and abscission of leaves and freeze damage to pineapple orange trees by freeze temperatures

Temperature	Ethylene evolution	Freeze damage		Leaf abscission
		Leaves	Twigs	
°F.	(a) [1]	Pct.	Pct.	Pct.
80	25	--	--	--
26	5,154	24	4	22
23	296	100	94	31
20	58	100	100	0

[1] Moles x 10^{-9}/g./24 hr. after thaw.

portions of peel; (4) homogenization; and (5) pasteurization at 190° to 205°F.; (6) and hot filling and cooling. Grapefruit puree was debittered by treating with 0.05 percent naringase (Kumitanase) before step 4 and holding the puree for 3 hours at 50° C. before step 5. The cloud properties of orange and grapefruit purees are listed in table 3. As little as 1 percent whole orange or grapefruit puree in sugar-citric acid-water solution produced a distinct cloud. Orange purees at the 10-percent level produced cloud values of approximately 20 percent T. Beverages prepared from pasteurized orange and grapefruit purees were considered to have acceptable qualities when prepared from purees stored for 6 months at ambient temperatures (60° to 95°F.).

DISCUSSION

QUESTION: Have you compared the flavor of the new deeply colored varieties with previous varieties?

MR. LIME: I don't think there is a difference in flavor at comparable maturity. The results of preliminary analysis indicate the Star Ruby matures 2 or 3 weeks later than the commerical varieties now grown in Texas. If Star Ruby and commercial samples were picked on the same date, the Star Ruby would have a higher acid value.

QUESTION: The new varieties are seedless, are they not?

MR. LIME: Yes, they are seedless. They make beautiful sections.

QUESTION: Were the leaves frozen in your cold chamber?

MR. LIME: Yes, for 4 hours at 26° F.

QUESTION: I'm surprised at the amount of damage to leaves at this temperature.

MR. LIME: The leaves were quite susceptible at this stage of growth. Actually, these tests were made by Dr. Roger Young and his group of Plant Science Research Division, they were checking for differences in ethylene production with different degrees of freeze damage. I'm sure that these tests were not comparable to grove conditions.

Table 3. Cloud properties of whole citrus purees in beverages — — Percent Transmission at 620 mu

	Range of cloud properties of — —			
Puree [1] (percent)	Marrs oranges	Hamlin oranges	Valencia oranges	Ruby grapefruit
1	90 to 94	85 to 93	81 to 91	96 to 97
5	41 to 51	42 to 50	31 to 48	73 to 87
10	21 to 23	20 to 21	16 to 24	46 to 54
15	15 to 19	14 to 17	13 to 16	28 to 35
20	12 to 14	11 to 13	10 to 12	20 to 25

[1] Puree mixed with solution of 0.75 percent C.A. and 12.5° Brix

PROGRESS REPORT ON POLLUTION CONTROL STUDY ON CITRUS FEED MILLS

by

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Under the auspices of the United States Department of Agriculture, a study of the emission of particulate matter and noxious or odorous gases from citrus feed mill driers is being made. Specifically, the investigation is toward type of mill and conditions of operation.

For purposes of the study, particulate matter determination is being made according to the conditions and by the methods prescribed by the State of Florida for measuring emissions for legal purposes.

The study is being conducted on three commercial feed mills of different basic design and is to extend over two citrus harvesting seasons.

A number of variable factors are being investigated as to their effect on the amount and character of emission: type of fuel, percentage of excess air, ambient temperature, and humidity.

Wherever applicable, tabulation is being made on volume and strength of liquid wastes produced; as in the case of waste heat evaporators condensate and barometric discharges.

Control of emissions to the atmosphere is now vested in the Florida Department of Air and Water Pollution Control, which assumed this activity from the Florida State Board of Health under the recent reorganization of State Agencies.

An examination of the statutory limits will serve well — both in definition of terms and in guidance to sampling methods.

An "Air Pollutant" is defined as "Any matter found in the atmosphere other than oxygen, nitrogen, water vapor, carbon dioxide, and the inert gases in natural concentrations."

The statute prohibits emission of particulate matter according to a graduated scale based upon weight of material input to process.

"Process Weight" is defined as "The total weight of all materials introduced into any process"; allowable discharge increases with input weight until a discharge level of 40 lb./hr. is reached, which is the maximum no matter how great the input.

Material input to process is peel weight plus lime.

The allowable emission is stated in pounds per hour per plant, not per stack.

The types of mill being studied are:

TYPE 1. DRYER — WASTE HEAT EVAPORATOR

Conventional furnace-dryer (with partial vapor recycle) is employed as heat source for shell and tube press water evaporator.

TYPE 2. DRYER — WASTE HEAT EVAPORATOR WITH REHEAT

Conventional furnace-dryer (with partial vapor recycle) is employed as heat source for shell and tube press water evaporator with reheat furnace for vapors after dryer.

TYPE 3. DRYER — SCRUBBER

Conventional furnace-dryer (with partial vapor recycle) is followed by scrubber employing press water as scrubbing liquid with scrub water returned to dryer inlet.

Six tests have been made, with two passing the State's requirements and four failing:

TYPE 1 was tested at normal capacity employing waste heat recovery — emissions were within allowable limits.

TYPE 1 was tested at reduced capacity with waste heat recovery apparatus being bypassed — emissions exceeded allowable limits.

TYPE 2 was tested at normal capacity employing waste heat recovery — emissions were within allowable limits.

TYPE 2 was tested at reduced capacity employing waste heat recovery — emissions exceeded allowable limits.

TYPE 3 was tested at normal capacity — emissions exceeded the allowable.

TYPE 3 was tested at normal capacity — emissions exceeded the allowable.

The machinery manufacturer (in Type 3) is modifying this installation by the addition of an additional dry cyclone and reducing velocity of stack to be similar to another of his mills which complies with emission requirements.

DISCUSSION

QUESTION: Are leaves removed from feed?

MR. SEABURY: No effort is made to segregate the leaves.

QUESTION: Is there a standard location for the stack emission sampler?

MR. SEABURY: Yes, according to specifications it should be two diameters below the top of the stack and at least eight diameters above the base and located at the point of average velocity for the stack gas.

QUESTION: What procedure is best when not using feed mill to full capacity?

MR. SEABURY: At low production rates it is best to let the moisture content rise to anywhere from 7.5 to 11 percent. This will guard against the emission of fines and the possible spontaneous combustion of the dried material.

Table 1. Preliminary results of testing to date

Mill type	Input	Moisture removal	Product	Condensate		Moisture		Emission	
				GPM	BOD	Peel	Product	Observed	Allowed
	No./hr.	No./hr.	No./hr.			Pct.	Pct.	No./Hr.	No./hr.
1	113,550	82,190	31,357	160	502	77.5	7.53	17.27	40.0
1	67,363	50,973	16,390	—	—	77.6	6.71	43.40	40.0
2	32,057	25,817	6,240	33	783	81.8	6.50	14.23	23.47
2	23,200	18,010	5,190	26	1020	78.8	5.14	18.88	18.12
3	16,814	13,534	3,280	0	0	81.7	6.08	75.35	14.24
3	17,335	14,345	2,990	0	0	84.5	10.0	38.90	14.56

PREPARATION AND USE OF CONCENTRATED ORANGE AROMA SOLUTIONS

by

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(Presented by M. K. Veldhuis)

Orange aroma solutions were prepared from commercial peel oil desludger effluents by stripping the oil and water soluble volatiles in a steam stripping unit and making a preliminary concentration of the volatile materials in a packed fractionating column. The runs were made with percent vaporization ranging from 5 to 23 percent and yields of oil and water soluble aroma were estimated. The more vaporization, the more oil and aroma were obtained. Generally, about 90 percent of the oil and 80 percent of the aroma were obtained with 10 percent vaporization. With more vaporization, some additional quantities of oil and aroma were obtained but the amount tapered off quite rapidly. As an example, with 13-percent vaporization, sufficient water soluble aroma was obtained to give good flavor to four volumes of reconstituted evaporator pump-out. By doubling the percent vaporization, enough aroma was obtained to flavor about six volumes of reconstituted pump-out.

The concentrated vapor fraction from the system was partly distilled orange oil and partly water soluble aromatics. When the system was operated in such a manner as to restrict the volume of the water phase, more of the aromatic material was to be found in the oil phase and vice versa. For example, in a series of runs when the volume of water was only half that of the oil, the total amount of aromatic material in the water phase from a given volume of centrifuge effluent would flavor only about an equal amount of evaporator pump-out. However, when the water to oil ratio was increased to 6 to 1, sufficient aromatic material was obtained from a given volume of centrifuge effluent to flavor 3 1/2 volumes of evaporator pump-out. The column can be operated to incease the yield in the aqueous phase if desired, depending upon whether one wants the bulk of the water soluble components in the oil or in the aqueous phase. In any case, the oil is quite aromatic as it is recovered in equilibrium with limited amount of the aqueous phase in comparison with cold-pressed oil (50 to 100 percent, w/o) or the usual distilled oil.

The aqueous phase from the original recovery system was concentrated in a packed column and concentrations of the aqueous phase were obtained in which one volume would flavor from 1,000 to 8,000 volumes of evaporator pump-out. These columns were simple devices and operated at atmospheric conditions in a continuous manner with a stripping section, a fractionating section, and a reflux splitter. By regulating the feed rate, the aromatic fraction was raised in concentration to folds ranging from 1,000 to over 8,000 and the flavor retention ranged from 83 to 96 percent measured by judging the amount of aromatic material required to flavor evaporator pump-out. The recovery was also judged by running COD values and in this case the range was from 55 to 98 percent. The high fold concentrations were attainable because the product was low in ethyl alcohol content in comparision with essence obtained from single strength juice.

One of the main purposes of the study was to obtain concentrations of flavoring materials which would be high enough so that they could be used in flavoring instant orange juice. That is, the product must be so concentrated that it will flavor the dehydrated product adequately without the introduction of sufficient water to increase the moisture content significantly. Satisfactory results were obtained when aromatic aqueous solutions were used of 3,000-fold and above. When used to flavor instant orange juice, the product was judged to be roughly equivalent to concentrated essence from orange juice and definitely improved the flavor of the reconstituted juice.

PILOT PLANT PREPARATION OF ORANGE PEEL COLOR

by

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(Presented by Charles W. Wilson, III)

Natural orange color concentrates separated from peel were obtained using a hexane extraction process modified for pilot plant scale production. Previous Citrus Conference reports have described a method developed on a laboratory scale for hexane extraction of color from orange peel. The methods involved a saponification step to remove materials interfering with flavor and color, and a steam distillation step to remove oil components. Previous reports included studies of peel batches of several kg., and reported yields of color from different varieties of fruit. Several modifications were made to enlarge the process to a pilot plant scale. Ratio of hexane to peel was reduced to 1:1 instead of the 2:1 proportions used in smaller scale experiments. Also, previous procedures had required extensive washing following the saponification step to remove excess base materials, soaps, and other precipitates formed during saponification. This extensive washing step was replaced by a neutralization wash with potassium acid phosphate. The incorporation of this step shortened the total time of the process by about one-half.

The process was also made more efficient by combining the two distillation steps which had been reported in earlier processes. In previous small-scale experiments, the product was vacuum distilled at one point to remove excess hexane. This was repeated at a later stage, followed by steam distillation to remove oil and flavor components which also was repeated. For larger scale pilot plant runs, it was found feasible to combine all these distillation steps separating oil and flavor components simultaneously with the hexane.

Using these developed improvements, this process was applied to 180-lb. units of FMC extractor whole peel, flavedo (obtained from an AMC Peel Shaver) and orange peel "frits" (ground peel and flavedo pieces expelled from an FMC In-Line Extractor). Color concentrates were prepared from three 180-lb. units of each of the three starting materials. Each 180-lb. unit was prepared by extracting three 60-lb. batches and combining the color extracts for subsequent processing. Yields of color were determined for each 180-lb. unit and averages were determined on the results from three units. Lowest average yields of color were obtained from "frits" and amounted to 30.9 g. color concentrate per 180-lb. frits (402 mg./kg.). Chopped whole peel yielded 43.9-g. color concentrate per 180-lb. peel (545 mg./kg.). Highest yields were obtained from ground flavedo 56.4-g. color concentrate per 180-lb. flavedo (669 mg./kg.).

Treatments were also developed for breaking up emulsions which form after the initial extraction step, and for obtaining additional yields of color from these emulsions. This process resulted in additional color which increased the total yield by 1 percent for color from whole peel, 30 percent for color from flavedo, and almost 50 percent for color from frits. Flavor studies on orange juice concentrates with color added indicated when it is blended with essence oil or distilled oil to make a reconstituted highly colored oil and this blended with juice at the desired level, very acceptable flavor quality results. Materials balance studies during these processes accounted for about 90 percent or more of the solids and indicated about 85 percent recovery of hexane. It is anticipated that this could be increased considerably by suitably designed commercial equipment. Hexane holdup in the extracted peel amounted to about 2 lb. hexane/100-lb. peel, and is probably sufficient to warrant steam distillation or other treatments to recover it. Cost studies indicate this process can be used to improve color by one grade point in juice reconstituted from 45° Brix FCOJ at an operating cost of less than one cent per 6-ounce can of concentrate. Several recently developed procedures for improving efficiency of the process can probably be used to lower operating costs even further.

DISCUSSION

QUESTION: Did you try alum to precipitate pectin from the emulsions?

MR. WILSON: Acetone was satisfactory, but alum might help. We tried lime but this caused excessive problems due to hardening of the peel.

QUESTION: Were there any off-flavors from acetone treatment of the emulsions?

MR. WILSON: There are literature references where off-flavors were produced when acetone was used in the presence of lipids. We have not checked this point, but we did not observe any off-flavor in the color from the emulsion.

QUESTION: How stable are color concentrates in FCOJ and single strength juice?

MR. WILSON: As long as the product remained frozen, the pigments were stable for over a year. In single strength juice they were stable up to 3 months at 50° F. or below, but at 70° and above they changed within a few weeks.

QUESTION: How was color added to products?

MR. WILSON: Color was blended with peel oil and the peel oil — color mixture was belended with the product.

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LIST OF CITRUS PUBLICATIONS AND PATENTS

(September 1, 1969 — August 31, 1970)

Reprints of publications may be obtained without cost by addressing request to the Laboratory listed.

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